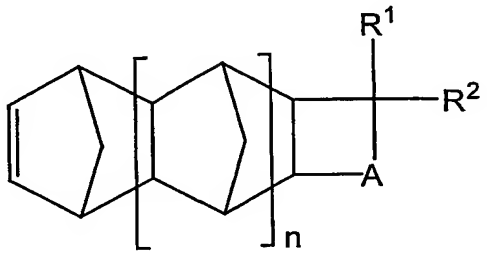
CLAIMS

What is claimed is:

1. An ethylenically unsaturated compound having the structure:



(I)

wherein n is 0, 1, or 2;

A is O or NR^3;

R^1 and R^2 are independently H; halogen; C_1 - C_{10} alkyl or alkoxy, optionally substituted by halogen or ether oxygen; C_6 - C_{20} aryl; Y; $C(R_f)(R_f')OR^4$; R^5Y; OR^5Y; and

R^3 is H; C_1-C_{10} alkyl or alkoxy, optionally substituted by halogen or ether oxygens; C_6-C_{20} aryl; Y; $C(R_f)(R_f')OR^4$; R^5Y;OR^5Y; or

R^1 and R^2 taken together are $=C(R_f)(R_f')$ or C_2-C_9 alkylene, optionally substituted by halogen or incorporating an ether oxygen; or

R^2 and R^3 taken together are part of a double bond;

Y is COZ or SO_2Z;

R^4 is hydrogen or an acid-labile protecting group;

R_f and R_f' are the same or different fluoroalkyl groups of 1 to 10 carbon atoms or taken together are $(CF_2)_m$ where m is 2 to 10;

R^5 is a C_1-C_{20} alkylene group, optionally substituted by halogen or ether oxygen;

Z is OH, halogen, R^6 or OR^6; and

R^6 is a C_1-C_{20} alkyl group, optionally substituted by halogen or ether oxygens; or C_6-C_{20} aryl;

with the proviso that at least one of R^1 or R^2 is fluorine or contains one or more fluorine atoms.

2. The ethylenically unsaturated compound of Claim 1, wherein n is 0 and A is oxygen.

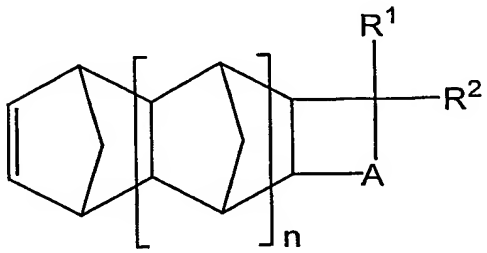
3. The ethylenically unsaturated compound of Claim 2, wherein R^1 and R^2 are perfluoroalkyl groups of 1 to 10 carbon atoms or taken together are $(CF_2)_m$ where m is 2 to 10.

4. The ethylenically unsaturated compound of Claim 2, wherein R^1 is CF_3 and R^2 is $COOR^6$.

5. A copolymer comprising:

(a) at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom, and

(b) at least one repeat unit derived from an ethylenically unsaturated compound having the structure:



(I)

wherein n is 0, 1, or 2;

A is O or NR^3;

R^1 and R^2 are independently H; halogen; C_1 - C_{10} alkyl or alkoxy, optionally substituted by halogen or ether oxygen; C_6 - C_{20} aryl; Y; $C(R_f)(R_f')OR^4$; R^5Y; OR^5Y; and

R^3 is H; C_1-C_{10} alkyl or alkoxy, optionally substituted by halogen or ether oxygens; C_6-C_{20} aryl; Y; $C(R_f)(R_f')OR^4$; R^5Y;OR^5Y; or

R^1 and R^2 taken together are $=C(R_f)(R_f')$ or C_2-C_9 alkylene, optionally substituted by halogen or incorporating an ether oxygen; or

R^2 and R^3 taken together are part of a double bond;

Y is COZ or SO_2Z;

R^4 is hydrogen or an acid-labile protecting group;

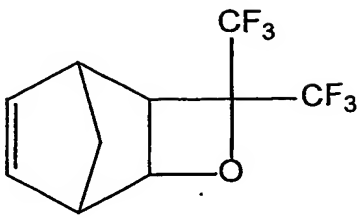
R_f and R_f' are the same or different fluoroalkyl groups of 1 to 10 carbon atoms or taken together are $(CF_2)_m$ where m is 2 to 10;

R^5 is a C_1-C_{20} alkylene group, optionally substituted by halogen or ether oxygen;

Z is OH, halogen, R^6 or OR^6; and

R^6 is a C_1-C_{20} alkyl group, optionally substituted by halogen or ether oxygens; or C_6-C_{20} aryl.

6. The copolymer of Claim 5, wherein (b) is selected from the group consisting of:



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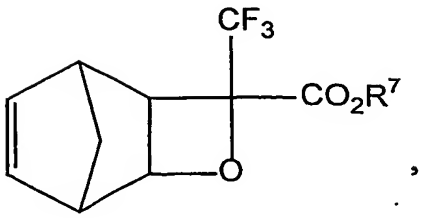

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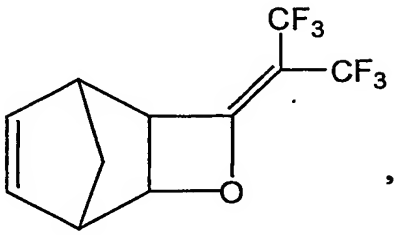

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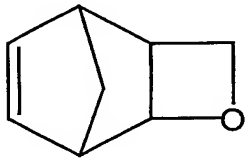

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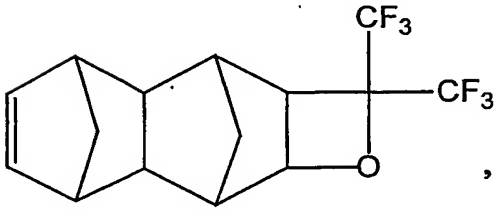

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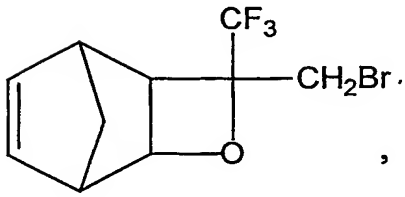

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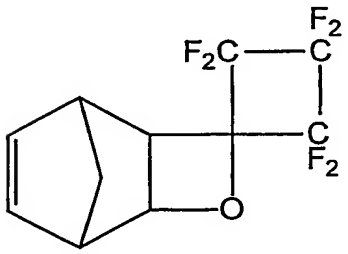

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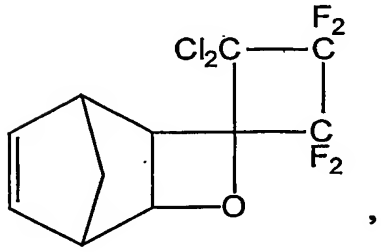

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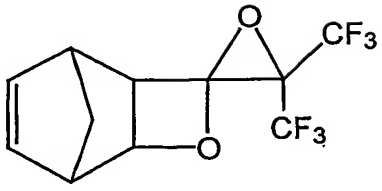
and



wherein R^7 is an alkyl group of 1 to 20 carbon atoms.

7. The copolymer of Claim 5, wherein (a) is a fluoroolefin comprising 2 to 20 carbon atoms.

8. The copolymer of Claim 7, wherein the fluoroolefin is selected from the group consisting of tetrafluoroethylene; hexafluoropropylene;

chlorotrifluoroethylene; vinylidene fluoride; vinyl fluoride; perfluoro-(2,2-dimethyl-1,3-dioxole); perfluoro-(2-methylene-4-methyl-1,3-dioxolane); $CF_2=CFO(CF_2)_tCF=CF_2$, wherein t is 1 or 2; and $R_f"OCF=CF_2$, wherein $R_f"$ is a saturated fluoroalkyl group of from 1 to 10 carbon atoms.

9. The copolymer of Claim 7, wherein the fluoroolefin is tetrafluoroethylene.

10. The copolymer of Claim 5, further comprising a fluoroalcohol group or a protected fluoroalcohol group.

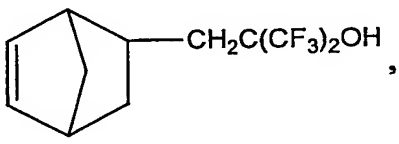
11. The copolymer of Claim 10, wherein the fluoroalcohol group or the protected fluoroalcohol group is derived from at least one ethylenically unsaturated compound containing a fluoroalcohol group having the structure:

$$-C(R_f)(R_f')OH$$

wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms, or taken together are $(CF_2)_n$ wherein n is 2 to 10.

12. The copolymer of Claim 11, wherein R_f and R_f' are perfluoroalkyl groups.

13. The copolymer of Claim 10, wherein the fluoroalcohol group or a protected fluoroalcohol group is derived from a monomer selected from the group consisting of:



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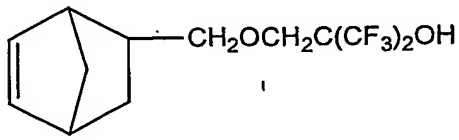

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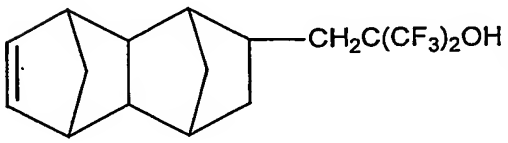

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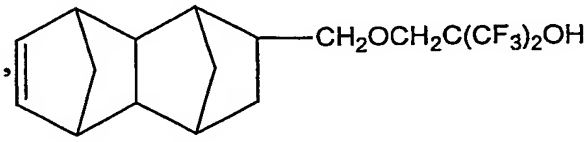

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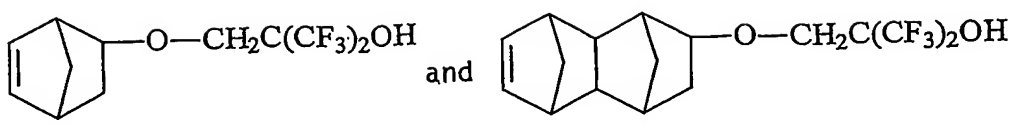
$CH_2=CHOCH_2CH_2OCH_2C(CF_3)_2OH$, $CH_2=CHO(CH_2)_4OCH_2C(CF_3)_2OH$,



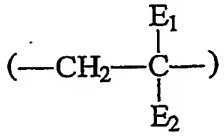
14. The copolymer of Claim 5, further comprising a fluoroalcohol group of structure:

$$-XCH_2C(R_f)(R_f')OH$$

wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms, or taken together are $(CF_2)_m$ wherein m is 2 to 10; and X is an element from Group VA and VIA of the Periodic Table of the Elements.

15. The copolymer of Claim 14, wherein X is selected from the group consisting of oxygen, sulfur, nitrogen and phosphorous.

16. The copolymer of Claim 5, further comprising at least one acid-containing or protected acid-containing structural unit:



wherein E_1 is H or C_1-C_{12} alkyl; E_2 is CO_2E_3, SO_3E, or other acidic group; and E and E_3 are H, or unsubstituted or heteroatom-substituted C_1-C_{12} alkyl.

17. The copolymer of Claim 16, wherein the heteroatom is selected from the group consisting of oxygen, nitrogen, sulfur, halogen and phosphorus.

18. The copolymer of Claim 17, wherein the heteroatom is oxygen, and the substituent further contains a hydroxyl group.

19. The copolymer of Claim 16, wherein the acid-containing or protected acid-containing structural unit comprises a carboxylic acid group.

20. The copolymer of Claim 16, wherein the acid-containing or protected acid-containing structural unit is derived from a monomer selected from the group consisting of tert-butyl acrylate; 2-methyl-2-adamantyl acrylate; 2-methyl-2-norbornyl acrylate; acrylic acid; methyl acrylate; ethyl acrylate; propyl acrylate; 2-hydroxyethyl acrylate; 2-methoxyethyl acrylate; 2-cyanoethyl acrylate; glycidyl acrylate and 2,2,2-trifluoroethyl acrylate.

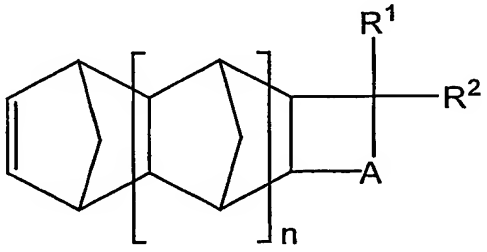
21. The copolymer of Claim 5, further comprising at least one polar monomer.

22. A photoresist composition comprising:

(a) a fluorine-containing copolymer comprising:

(i) at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom; and

(ii) at least one repeat unit derived from an ethylenically unsaturated cyclic compound having the structure:



(I)

wherein n is 0, 1, or 2;

A is O or NR^3;

R^1 and R^2 are independently H; halogen; C_1 - C_{10} alkyl or alkoxy, optionally substituted by halogen or ether oxygen; C_6 - C_{20} aryl; Y; $C(R_f)(R_f')OR^4$; R^5Y; OR^5Y; and

R^3 is H; C_1-C_{10} alkyl or alkoxy, optionally substituted by halogen or ether oxygens; C_6-C_{20} aryl; Y; $C(R_f)(R_f')OR^4$; R^5Y;OR^5Y; or

R^1 and R^2 taken together are $=C(R_f)(R_f')$ or C_2-C_9 alkylene, optionally substituted by halogen or incorporating an ether oxygen; or

R^2 and R^3 taken together are part of a double bond;

Y is COZ or SO_2Z;

R^4 is hydrogen or an acid-labile protecting group;

R_f and R_f' are the same or different fluoroalkyl groups of 1 to 10 carbon atoms or taken together are $(CF_2)_m$ where m is 2 to 10;

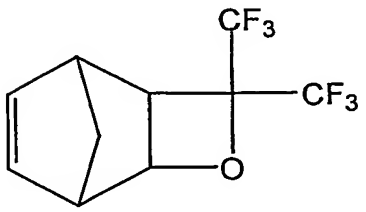
R^5 is a C_1-C_{20} alkylene group, optionally substituted by halogen or ether oxygen;

Z is OH, halogen, R^6 or OR^6; and

R^6 is a C_1-C_{20} alkyl group, optionally substituted by halogen or ether oxygens; or C_6-C_{20} aryl; and

(b) a photoactive component.

23. The photoresist composition of Claim 22, wherein (ii) is selected from the group consisting of:



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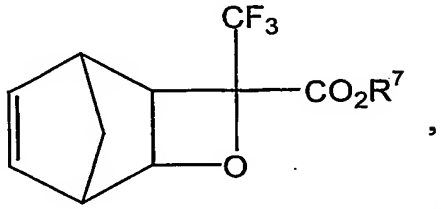

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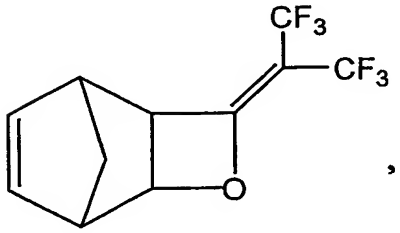

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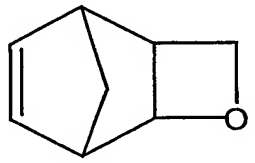

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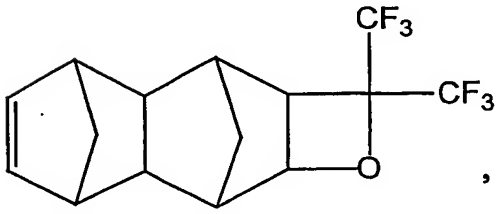

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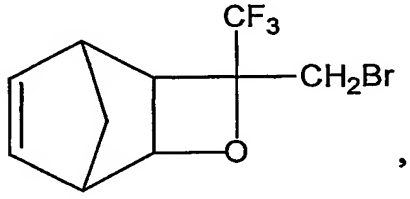

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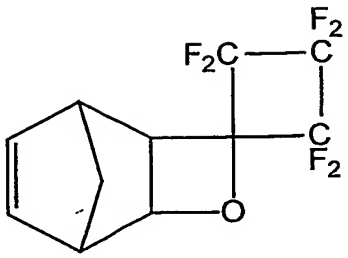

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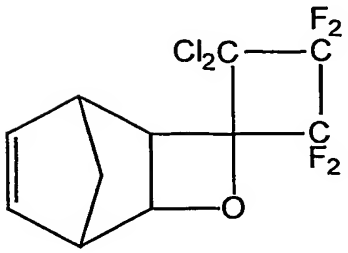

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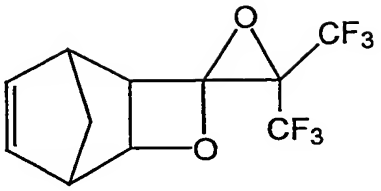


wherein R^7 is an alkyl group of 1 to 20 carbon atoms.

24. The photoresist composition of Claim 22, wherein (i) is a fluoroolefin comprising 2 to 20 carbon atoms.

25. The photoresist composition of Claim 24, wherein the fluoroolefin is selected from the group consisting of tetrafluoroethylene; hexafluoropropylene; chlorotrifluoroethylene; vinylidene fluoride; vinyl fluoride; perfluoro-(2,2-dimethyl-1,3-dioxole); perfluoro-(2-methylene-4-methyl-1,3-dioxolane); $CF_2=CFO(CF_2)_tCF=CF_2$, wherein t is 1 or 2; and $R_f"OCF=CF_2$, wherein $R_f"$ is a saturated fluoroalkyl group of from 1 to about ten carbon atoms.

26. The photoresist composition of Claim 25, wherein the fluoroolefin is tetrafluoroethylene.

27. The photoresist composition of Claim 22, wherein the fluorine-containing copolymer further comprises a fluoroalcohol group or a protected fluoroalcohol group.

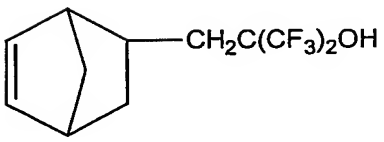
28. The photoresist composition of Claim 27, wherein the fluoroalcohol group or the protected fluoroalcohol group is derived from at least one ethylenically unsaturated compound containing a fluoroalcohol group having the structure:

$$-C(R_f)(R_f')OH$$

wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms or taken together are $(CF_2)_n$ wherein n is 2 to 10.

29. The photoresist composition of Claim 28, wherein R_f and R_f' are perfluoroalkyl groups.

30. The photoresist composition of Claim 28, wherein the fluoroalcohol group is derived from a monomer selected from the group consisting of:



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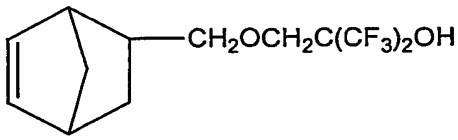

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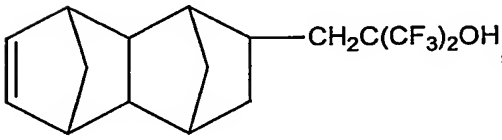

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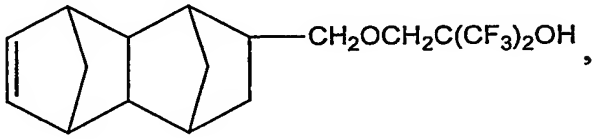

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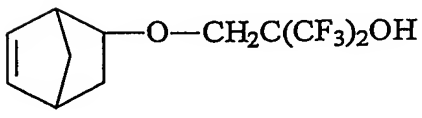
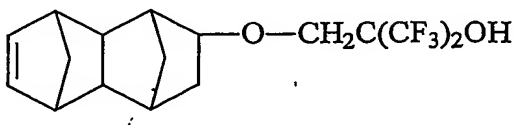
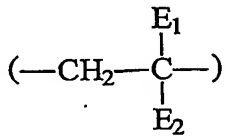
CH_2=CHO$CH_2CH_2OCH_2C(CF_3)_2OH$, CH_2=CHO$(CH_2)_4OCH_2C(CF_3)_2OH$,



and



31. The photoresist composition of Claim 22, wherein the fluorine-containing copolymer further comprises at least one acid-containing or protected acid-containing structural unit:



wherein E_1 is H or C_1-C_{12} alkyl; E_2 is CO_2E_3, SO_3E, or other acidic group; and E and E_3 are H or unsubstituted or heteroatom substituted C_1-C_{12} alkyl, with the proviso that if the heteroatom is oxygen, the substituent contains a hydroxyl group.

32. The photoresist composition of Claim 31, wherein the heteroatom is selected from the group consisting of oxygen, nitrogen, sulfur, halogen and phosphorus.

33. The polymer of Claim 32, wherein the heteroatom is oxygen, and the substituent further contains a hydroxyl group.

34. The photoresist composition of Claim 31, wherein the acid-containing or protected acid-containing structural unit comprises a carboxylic acid group.

35. The photoresist composition of Claim 34, wherein the acid-containing or protected acid-containing structural unit is derived from a monomer selected from the group consisting of tert-butyl acrylate; 2-methyl-2-adamantyl acrylate; 2-methyl-2-norbornyl acrylate; acrylic acid; methyl acrylate; ethyl acrylate; propyl acrylate; 2-hydroxyethyl acrylate; 2-methoxyethyl acrylate; 2-cyanoethyl acrylate; glycidyl acrylate and 2,2,2-trifluoroethyl acrylate.

36. The photoresist composition of Claim 22, wherein the fluorine-containing copolymer further comprises at least one polar monomer.

37. The photoresist composition of Claim 22, wherein the photoactive component is a photoacid generator.

38. The photoresist composition of Claim 22, further comprising a dissolution inhibitor.

39. The photoresist composition of Claim 22, further comprising a solvent.

40. The photoresist composition of Claim 39, wherein the solvent is selected from the group consisting of ether esters; ketones; esters; glycol ethers; unsubstituted and substituted hydrocarbons; aromatic hydrocarbons; fluorinated solvents and supercritical CO_2.

41. The photoresist composition of Claim 22, further comprising at least one additive selected from the group consisting of bases, surfactants, resolution enhancers, adhesion promoters, residue reducers, coating aids, plasticizers, and T_g (glass transition temperature) modifiers.

42. A coated substrate comprising:

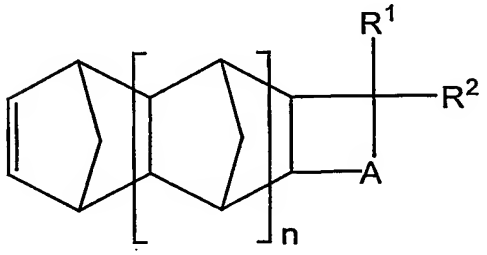
(a) a substrate; and

(b) a photoresist composition comprising a fluorine-containing copolymer comprising:

(i) a fluorine-containing copolymer comprising:

(a') at least one repeat unit derived from an ethylenically unsaturated compound having at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom; and

(b') at least one repeat unit derived from an ethylenically unsaturated cyclic compound having the structure:



(I)

wherein n is 0, 1, or 2;

A is O or NR^3;

R^1 and R^2 are independently H; halogen; C_1 - C_{10} alkyl or alkoxy, optionally substituted by halogen or ether oxygen; C_6 - C_{20} aryl; Y; $C(R_f)(R_f')OR^4$; R^5Y; OR^5Y; and

R^3 is H; C_1-C_{10} alkyl or alkoxy, optionally substituted by halogen or ether oxygens; C_6-C_{20} aryl; Y; $C(R_f)(R_f')OR^4$; R^5Y;OR^5Y; or

R^1 and R^2 taken together are $=C(R_f)(R_f')$ or C_2-C_9 alkylene, optionally substituted by halogen or incorporating an ether oxygen; or

R^2 and R^3 taken together are part of a double bond;

Y is COZ or SO_2Z;

R^4 is hydrogen or an acid-labile protecting group;

R_f and R_f' are the same or different fluoroalkyl groups of 1 to 10 carbon atoms or taken together are $(CF_2)_m$ where m is 2 to 10;

R^5 is a C_1-C_{20} alkylene group, optionally substituted by halogen or ether oxygen;

Z is OH, halogen, R^6 or OR^6; and

R^6 is a C_1-C_{20} alkyl group, optionally substituted by halogen or ether oxygens; or C_6-C_{20} aryl; and

(ii) a photoactive component.

43. The coated substrate of Claim 42, wherein the substrate is a microelectronic wafer.

44. The coated substrate of Claim 43, wherein the microelectronic wafer is comprises a material selected from the group consisting of silicon, silicon oxide, silicon oxynitride, and silicon nitride.